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2′-*p*-METHOXYCOUMAROYLALOERESIN, A *C*-GLUCOSIDE FROM *ALOE EXCELSA*

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Key Word Index—*Aloe excelsa*; Liliaceae; aloesin; *C*-glucosides; *p*-methoxycoumaroylaloeresin.

Abstract—The leaves of *Aloe excelsa* afforded, aloesin, anthraquinones and a new compound 2′-*p*-methoxycoumaroylaloeresin whose structure, 2-acetonyl-7-hydroxy-8-*C*-β-D-[2′-*O*-(*E*)-*p*-methoxycoumaroyl]-methylchromone, was established by spectral and chemical means.

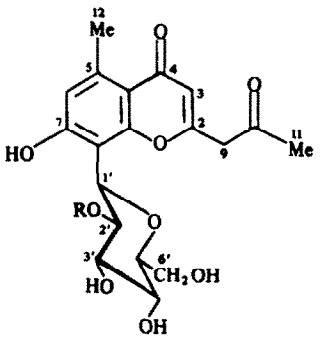
INTRODUCTION

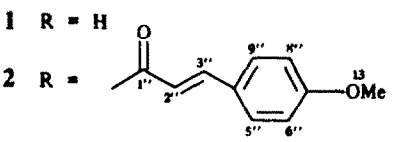
The leaves of *Aloe excelsa* A. Berger, which is widely distributed in southern Africa, are commonly used in traditional medicine to treat venereal sores, asthma and abdominal pains [1]. Many aloe species contain anthraquinones, anthrones, chromones and their *C*-glycosyl derivatives [2–4]. I report here a chemical investigation of the dried leaf surfaces of *Aloe excelsa* which resulted in the isolation of a new natural compound, *p*-methoxycoumaroylaloeresin (**2**) and known compounds, aloesin (**1**) [5], homonataloin [6], aloin [4] and 1,5-dihydroxy-3-hydroxymethylanthraquinone [7] from the acetone extract.

RESULTS AND DISCUSSION

The compound **2**, $C_{29}H_{30}O_{11}$, gave a dark green colour with ferric chloride and dissolved in aqueous sodium hydroxide indicating its phenolic nature. The IR spectrum showed two carbonyl bands at 1652 and 1716 cm^{-1} and an hydroxyl group band at 3340 cm^{-1}. The UV spectrum had maxima at 226, 250 (sh) and 297 nm. Both spectra correspond closely with those of **1**. The presence of the aloesin system is supported by the ^1H NMR spectrum (CD_3COCD_3), which showed three singlets at δ2.36, 2.74 and 3.94 for the acetonyl, aromatic and methoxyl methyl groups, respectively. The D_2O exchangeable singlet at δ10.00 was attributed to the unchelated phenolic hydroxyl group. The glucosyl protons appeared as multiplets at δ3.40–3.90 and the methylene protons of the acetonyl group appeared as a singlet at δ3.84. The singlets at δ6.18 and 6.85 were ascribed to the olefinic proton (H-3) and the aromatic proton (H-6), respectively. The remaining ^1H NMR signals at δ3.94 (*s*, OMe) and a set at 6.08 (*d*, J = 16 Hz, 1H) and 7.36 (*d*, J = 16 Hz 1H) (typical AB pattern of *trans* olefinic protons) and another set at 6.88 (*d*, J = 8.6 Hz, 2H) and 7.48 (*d*, J = 8.6 Hz, 4H) (typical AA′BB′ pattern of a 1,4-disubstituted aromatic compound) and the ^{13}C NMR data (Experimental) indicated the substitution of an (*E*)-*p*-methoxycoumaroyl unit in the aloesin parent structure. The position of the *p*-methoxycoumaroyl unit was deduced from the most deshielded triplet peak at δ5.68 which was assigned to a glucosyl proton on the acylated carbon [8]. The acylation position was determined to be at C-2′ by a spin decoupling experiment. Irradiation of a doublet peak at δ5.16 (H-1′), second most deshielded, simplified only the triplet peak at δ5.68 to a doublet. This signal was assigned to the proton H-2′ of the acylated carbon.

Definitive proof of the principal structure was obtained from hydrolysis of **2** with sodium methoxide in methanol, which afforded **1**, identified by co-TLC and mmp with an authentic sample, and *p*-methoxycoumaric acid, identified by its ^1H NMR and MS data analysis. The results of the





hydrolysis further proved that the methoxyl group is attached to the coumaroyl unit (C-7″) and not to the aloesin system (C-7). Further support for structure **2** was obtained from its mass spectrum which/shows the molecular ion peak at *m/z* 554, loss of the *p*-methoxycoumaric acid at *m/z* 376 and the presence of the *p*-methoxycoumaroyl fragment ion at *m/z* 161.

EXPERIMENTAL

Leaves of *Aloe excelsa* collected from the University of Zimbabwe campus, Harare, Zimbabwe were skinned. The skins were air-dried, powdered and extracted with Me_2CO. After removal of the solvent, the extract was subjected to CC over silica gel when **2** was obtained with MeOH–$CHCl_3$ (1:3). The known *C*-glucosides were obtained in larger quantities by CC using H_2O–MeOH–$CHCl_3$ (1:14:10) as eluent. The red pigment; 1,5-dihydroxy-3-hydroxymethylanthraquinone [7] was obtained from prep. TLC with MeOH–$CHCl_3$ (1:9) from the $CHCl_3$ extract of the Me_2CO residue. All isolated known compounds were identified by direct comparison (mmp, TLC, and ^{1}H NMR) with authentic samples.

2′-p-*Methoxycoumaroylaloeresin* (**2**). **2** was recryst. from EtOAc as light yellow crystals, mp 138–140°, soluble in Na_2CO_3 and NaOH soln. UV λ_{max}^{EtOH} nm (log): 226 (4.41), 251 sh (3.90), 298 (4.14); IR ν_{max}^{KBr} cm^{-1}: 3340, 1716, 1652, 1602, 1515, 1460, 1380, 1166, 916, 835, 759. ^{1}H NMR (Me_2CO-d_6): δ2.35 (*s*, 3H, aromatic methyl), 2.74 (*s*, 3H, acetonyl methyl), 3.45–4.00 (*m*, 8H, glucosyl protons), 3.86 (*s*, 2H acetonyl methylene), 3.94 (*s*, 3H, aromatic methoxyl), 5.16 (*d*, 1H, H-1′), 5.69 (*t*, 1H, H-2′), 6.08 (*d*, 1H, H-2″), 6.18 (*s*, 1H, H-3), 6.85 (*s*, 1H, H-6), 6.88 (*d*, 2H, H-6 and H-8″), 7.35 (*d*, 1H, H-3″), 7.48 (*d*, 2H, H-5″) and H-9″), 9.90 [*s br*, 1H, phenolic proton]. ^{13}C NMR (DMSO-d_6): δ22.7 (C-12), 29.7 (C-11), 48.3 (C-9), 55.9 (C-13), 61.5 (C-6′), 70.4 (C-1′), 70.6 (C-4′), 72.1 (C-2′), 77.8 (C-3′) 81.8 (C-5′), 110.8 (C-8), 112.8) (C-3), 114.6 (C-2″), 115.6 (C-6″, 8″), 115.7 (C-4a), 116.8 (C-6), 125.0 (C-4″), 130.1 (C-5″, 9″) 141.8 (C-5), 144.6 (C-3″), 157.4 (C-1a), 159.7 (C-7), 160.6 (C-2), 161.3 (C-7″), 165.4 (C-1″), 178.6 (C-4), 202.1 (C-10). MS *m/z* (rel. int.): 554 ([M]$^+$, 15), 408 (2), 376 ([M – $C_{10}H_{10}O_3$], 2), 341 (7), 275 (100), 259 (14), 256 (47), 233 (61), 193 (15), 178 (4), 161 (8).

Alkaline hydrolysis. **2** was dissolved in 1% KOH in MeOH and soln was refluxed for 2 hr. After evap. of MeOH, the residue was diluted with H_2O and acidified with dil HCl. The soln was first extracted with Et_2O and then *n*-BuOH. The Et_2O extract, after chromatography, showed a molecular ion *m/z* 178 in the MS and the same ^{1}H NMR spectrum as (*E*)-*p*-methoxycoumaric acid, while the *n*-BuOH extract showed the same UV spectrum and chromatographic behaviour as **1**.

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